

**POLYMER WITH PENDENT CYCLIC OLEFINIC FUNCTIONS  
FOR OXYGEN SCAVENGING PACKAGING**

**FIELD OF THE INVENTION**

The present invention relates to compositions for use in areas such as food packaging, and with minimal effect on odor and taste of packaged contents.

The invention preferably uses ethylene acrylate copolymers which are modified with selected <sup>cyclic olefinic</sup> cyclic allylic pendent groups for use in oxygen scavenging packaging materials.

**BACKGROUND OF THE INVENTION**

New polymer compositions having properties that are particularly tailored for specific applications are required in response to more specific and sophisticated end uses. It can be difficult to make these compositions directly by polymerization from monomers or via solution esterification or transesterification, but manufacturing them in melt mixing equipment such as an extruder has provided an efficient, economical and viable means to supply increasingly complex polymers to meet the needs in specialized markets.

It is well known that regulating the exposure of oxygen-sensitive products to oxygen maintains and enhances the quality and "shelf-life" of the product. For instance, by limiting the exposure of oxygen sensitive food products to oxygen in a packaging system, the quality or freshness of food is maintained, spoilage reduced and the food shelf life extended. In the food packaging industry, several means for regulating oxygen exposure have already been developed. These means include modified atmosphere packaging (MAP) and oxygen barrier film packaging.

One method currently being used is "active packaging", whereby the package containing the food product has been modified in some manner to regulate

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1 the food's exposure to oxygen. One form of active packaging uses oxygen-  
2 scavenging sachets which contain a composition which scavenges the  
3 oxygen through oxidation reactions. One type of sachet contains iron-based  
4 compositions which oxidize to their ferric states. Another type of sachet  
5 contains unsaturated fatty acid salts on a particulate adsorbent. Yet another  
6 sachet contains metal/polyamide complex. However, one disadvantage of  
7 sachets is the need for additional packaging operations to add the sachet to  
8 each package. A further disadvantage arising from the iron-based sachets is  
9 that certain atmospheric conditions (e.g., high humidity, low CO<sub>2</sub> level) in the  
10 package are sometimes required in order for scavenging to occur at an  
11 adequate rate. Further, the sachets can present a problem to consumers if  
12 accidentally ingested.

13 Another means for regulating exposure of a packaged product to oxygen  
14 involves incorporating an oxygen scavenger into the packaging structure  
15 itself. A more uniform scavenging effect through the package is achieved by  
16 incorporating the scavenging material in the package instead of adding a  
17 separate scavenger structure (e.g., a sachet) to the package. This may be  
18 especially important where there is restricted airflow inside the package. In  
19 addition, incorporating the oxygen scavenger into the package structure  
20 provides a means of intercepting and scavenging oxygen as it permeates the  
21 walls of the package (herein referred to as an "active oxygen barrier"), thereby  
22 maintaining the lowest possible oxygen level in the package.

23 One attempt to prepare an oxygen-scavenging wall involves the incorporation  
24 of inorganic powders and/or salts. However, incorporation of these powders  
25 and/or salts causes reduction of the wall's optical transparency, discoloration  
26 after oxidation, and reduced mechanical properties such as tear strength. In  
27 addition, these compounds can lead to processing difficulties, especially when  
28 fabricating thin films. The oxidation products may migrate into food at levels  
29 which would not be regarded as safe or can impart unacceptable taste or  
30 smell to food.

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1 An oxygen-scavenging composition comprising a blend of a first polymeric  
2 component comprising a polyolefin is known, the first polymeric component  
3 having been grafted with an unsaturated carboxylic anhydride or an  
4 unsaturated carboxylic acid, or combinations thereof, or with an epoxide; a  
5 second polymeric component having -OH, -SH, or -NHR<sup>2</sup> groups where R<sup>2</sup> is  
6 H, C<sub>1</sub>-C<sub>3</sub> alkyl, substituted C<sub>1</sub>-C<sub>3</sub> alkyl; and a catalytical amount of metal salt  
7 capable of catalyzing the reaction between oxygen and the second polymeric  
8 component, the polyolefin being present in an amount sufficient so that the  
9 blend is not phase-separated. A blend of polymers is utilized to obtain oxygen  
10 scavenging, and the second polymeric component is preferably a polyamide  
11 or a copolyamide such as the copolymer of m-xylylene-diamine and adipic  
12 acid (MXD6).

13 Some oxygen scavenging systems produce an oxygen-scavenging wall. This  
14 is done by incorporating a metal catalyst-polyamide oxygen scavenging  
15 system into the package wall. Through catalyzed oxidation of the polyamide,  
16 the package wall regulates the amount of oxygen which reaches the interior  
17 volume of the package (active oxygen barrier) and has been reported to have  
18 oxygen scavenging rate capabilities up to about 5 cubic centimeters (cc)  
19 oxygen per square meter per day at ambient conditions. However, this  
20 system suffers from significant disadvantages.

21 One particularly limiting disadvantage of polyamide/catalyst materials can be  
22 a low oxygen scavenging rate. Adding these materials to a high-barrier  
23 package containing air can produce a package which is not generally suitable  
24 for creating an internal oxygen level of less than 0.1% within seven days at  
25 storage temperatures, as is typically required for headspace oxygen  
26 scavenging applications.

27 There are also disadvantages to having the oxygen-scavenging groups in the  
28 backbone or network structure in this type of polyamide polymer. The basic  
29 polymer structure can be degraded and weakened upon reaction with oxygen.

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1 This can adversely affect physical properties such as tensile or impact  
2 strength of the polymer. The degradation of the backbone or network of the  
3 polymer can further increase the permeability of the polymer to those  
4 materials sought to be excluded, such as oxygen.

5 Moreover, polyamides previously used in oxygen scavenging materials, such  
6 as MXD6, are typically incompatible with thermoplastic polymers used in most  
7 flexible packaging walls, such as ethylene-vinyl acetate copolymers and low  
8 density polyethylene. Even further, when such polyamides are used by  
9 themselves to make a flexible package wall, they may result in inappropriately  
10 stiff structures. They also incur processing difficulties and higher costs when  
11 compared with the costs of thermoplastic polymers typically used to make  
12 flexible packaging. Even further, they are difficult to heat seal. Thus, all of  
13 these are factors to consider when selecting materials for packages,  
14 especially multi-layer flexible packages and when selecting systems for  
15 reducing oxygen exposure of packaged products.

16 Another approach to scavenging oxygen is an oxygen-scavenging  
17 composition comprising an ethylenically unsaturated hydrocarbon and a  
18 transition metal catalyst. Ethylenically unsaturated compounds such as  
19 squalene, dehydrated castor oil, and 1,2-polybutadiene are useful oxygen  
20 scavenging compositions, and ethylenically saturated compounds such as  
21 polyethylene and ethylene copolymers are used as diluents. Compositions  
22 utilizing squalene, castor oil, or other such unsaturated hydrocarbon typically  
23 have an oily texture as the compound migrates toward the surface of the  
24 material. Further, polymer chains which are ethylenically unsaturated in the  
25 backbone would be expected to degrade upon scavenging oxygen,  
26 weakening the polymer due to polymer backbone breakage, and generating a  
27 variety of off-odor/off-taste by-products.

28 Other oxidizable polymers recognized in the art include "highly active"  
29 oxidizable polymers such as poly(ethylene-methyl acrylate-benzyl acrylate),

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1 EMBZ, and poly(ethylene-methyl acrylate-tetrahydrofurfuryl acrylate), EMTF,  
2 as well as poly(ethylene-methyl acrylate-nopol acrylate), EMNP. Although  
3 effective as oxygen scavengers, these polymers have the drawback of giving  
4 off large amounts of volatile by-products and/or strong odors after oxygen  
5 scavenging.

6 Also known are oxygen-scavenging compositions which comprise a transition-  
7 metal salt and a compound having an ethylenic backbone and having allylic  
8 pendent or terminal moieties which contain a carbon atom that can form a free  
9 radical that is resonance-stabilized by an adjacent group. Such a polymer  
10 needs to contain a sufficient amount and type of transition metal salt to  
11 promote oxygen scavenging by the polymer when the polymer is exposed to  
12 an oxygen-containing fluid such as air. Although effective as oxygen  
13 scavengers, upon oxidation, we have found that allylic pendent groups on an  
14 ethylenic backbone tend to generate considerable amounts of organic  
15 fragments. We believe this is a result of oxidative cleavage. We believe  
16 these fragments can interfere with the use of allylic pendent groups as oxygen  
17 scavengers in food packaging.

18 The present invention solves many of the problems of the prior art, especially  
19 with an oxygen scavenging packaging material incorporating polymers  
20 comprising cyclic allylic (olefinic) pendent groups which produce little or no  
21 migration of oxidation by-products adversely affecting odor or taste, thus  
22 minimizing organoleptic problems in food packaging. This is because the  
23 cyclic allylic structures are less likely to fragment or cleave after oxidation than  
24 the conventional open chain allylic (olefinic) groups used in oxygen  
25 scavenging packaging material.

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SUMMARY OF THE INVENTION

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2 According to the present invention, a <sup>compound</sup> composition is provided comprising a  
3 polymeric backbone, cyclic olefinic pendent groups and linking groups linking  
4 the olefinic pendent groups to the polymeric backbone.

5 Also according to the present invention, an oxygen scavenging <sup>compound</sup> composition is  
6 provided comprising a polymeric backbone, cyclic olefinic pendent groups,  
7 linking groups linking the olefinic pendent groups to the polymeric backbone  
8 and a transition metal catalyst.

9 Also according to the present invention, an article of manufacture is provided  
10 which is suitable as a container, the container inhibiting oxidation of contents  
11 of the container by removing oxygen from the container and by inhibiting  
12 ingress of oxygen into the container from outside the container, the article  
13 comprising an oxygen scavenging <sup>compound</sup> composition which comprises a polymeric  
14 backbone, cyclic olefinic pendent groups, linking groups linking the olefinic  
15 pendent groups to the backbone, and a transition metal catalyst.

16 Also according to the present invention, a layer suitable for scavenging  
17 oxygen is provided which comprises (a) a polymer backbone; (b) cyclic  
18 olefinic pendent groups; (c) linking groups linking the backbone with the  
19 pendent groups; and (d) a transition metal catalyst.

20 Also according to the present invention, a process of making a polymer  
21 material is provided, the process being selected from the group consisting of  
22 esterification, transesterification, amidation, transamidation and direct  
23 polymerization, in which the oxygen scavenging packaging material  
24 comprises a polymer backbone, cyclic olefinic pendent groups, linking groups  
25 linking the backbone with the pendent groups.

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1 In a preferred embodiment of the invention, the polymeric backbone of the  
2 above <sup>Compound</sup> compositions, article, layer and process is ethylenic and the linking  
3 groups are selected from the group consisting of:

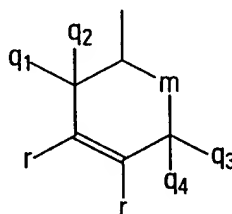
4  $-O-(CHR)_n-$ ;  $-(C=O)-O-(CHR)_n-$ ;  $-NH-(CHR)_n-$ ;  $-O-(C=O)-(CHR)_n-$ ;

5  $-(C=O)-NH-(CHR)_n-$ ; and  $-(C=O)-O-CHOH-CH_2-O-$ ;

6 wherein R is hydrogen or an alkyl group selected from the group consisting of  
7 methyl, ethyl, propyl and butyl groups and where n is an integer in the range  
8 from 1 to 12.

9 In a more preferred embodiment of the invention, the cyclic olefinic pendent  
10 groups of the above <sup>Compound</sup> compositions, article, layer and process have the  
11 structure (I):

12 (I)



15 where  $q_1$ ,  $q_2$ ,  $q_3$ ,  $q_4$ , and  $r$  are selected from the group consisting of  $-H$ ,  $-CH_3$ ,  
16 and  $-C_2H_5$ ; and where  $m$  is  $-(CH_2)_n-$  with  $n$  being an integer in the range from  
17 0 to 4; and wherein, when  $r$  is  $-H$ , at least one of  $q_1$ ,  $q_2$ ,  $q_3$  and  $q_4$  is  $-H$ .

18 In another preferred embodiment of the invention, the polymeric backbone of  
19 the above <sup>Compound</sup> compositions, article, layer and process comprises monomers  
20 selected from the group consisting of ethylene and styrene.

21 In yet another preferred embodiment of invention, the cyclic olefinic pendent  
22 groups of the above <sup>Compound</sup> compositions, article, layer and process are grafted onto

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1 the linking groups of the polymeric backbone by a esterification,  
2 transesterification, amidation or transamidation reaction.

3 In still another preferred embodiment of the invention, the esterification,  
4 transesterification, amidation or transamidation reaction of the above  
5 ~~compositions~~ <sup>compound</sup>, article, layer and process is a solution reaction or a reactive  
6 extrusion.

7 In another preferred embodiment of the invention, the esterification,  
8 transesterification, amidation or transamidation reaction of the above  
9 ~~compositions~~ <sup>compound</sup>, article, layer and process is catalyzed by a catalyst selected  
10 from the group consisting of strong non-oxidizing acids, tertiary amines,  
11 Group I alkoxides, Group IVB alkoxides, and Group IVA organometallics.

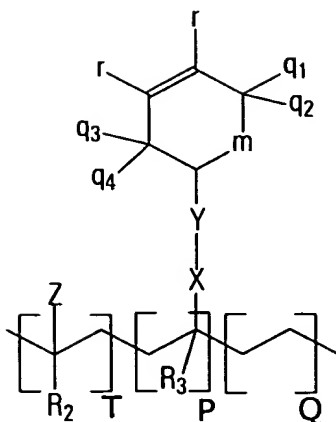
12 In yet another preferred embodiment of invention, the catalyst of the above  
13 ~~compositions~~ <sup>compound</sup>, article, layer and process is selected from a group consisting of  
14 toluene sulfonic acid, sodium methoxide, tetrabutyl titanate, tetraisopropyl  
15 titanate, tetra-n-propyl-titanate, tetraethyl titanate, 2-hydroxy-pyridine and  
16 dibutyltin dilaurate.

17 In still another preferred embodiment of the invention, the polymeric  
18 backbone, linking groups and cyclic olefin pendent groups of the above  
19 ~~compositions~~ <sup>compound</sup>, article, layer and process comprise repeating units, each unit  
20 having a structure (II) as follows:

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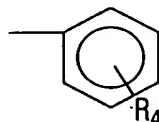


*Polymer*



(II)

wherein P+T+ Q is 100 mol % of the total composition; P is greater than 0 mol % of the total composition; Z is selected from the group consisting of an aryl group;  $-(C=O)OR_1$ ;  $-O(C=O)R_1$ ; and an alkyl aryl group:



where  $R_4$  is selected from the group consisting of  $-CH_3$ ,  $-C_2H_5$ , and  $-H$ ;  $R_1$  is selected from the group consisting of  $-H$ ,  $-CH_3$ ,  $-C_2H_5$ ,  $-C_3H_7$  and  $-C_4H_9$ ;  $R_2$  and  $R_3$  are selected from the group consisting of  $-H$  and  $-CH_3$ ; X is selected from the group consisting of  $-O-$ ,  $-NH-$ ,  $-(C=O)O-$ ,  $-(C=O)NH-$ ,  $-(C=O)S-$ ,  $-O(C=O)-$  and  $-(CHR)_\ell-$ ;  $\ell$  is an integer in the range from 1 to 6; Y is  $-(CHR)_n-$ , where n is an integer in the range from 0 to 12, R being selected from the group consisting of  $-H$ ,  $-CH_3$  and  $-C_2H_5$ ; where  $q_1$ ,  $q_2$ ,  $q_3$ ,  $q_4$ , and r are selected from the group consisting of  $-H$ ,  $-CH_3$ , and  $-C_2H_5$ ; and where m is  $-(CH_2)_n-$  and where n is an integer in the range from 0 to 4; and wherein when r is  $-H$ , at least one of  $q_1$ ,  $q_2$ ,  $q_3$  and  $q_4$  is  $-H$ .

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1 In another preferred embodiment of the invention, the cyclic olefinic pendent  
2 groups of the above <sup>compounds</sup> compositions, article, layer and process are selected  
3 from the group consisting of cyclohexene-4-methylene radical, 1-methyl  
4 cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-methylene radical,  
5 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl cyclohexene-4-  
6 methylene radical, 1,5-dimethyl cyclohexene-4-methylene radical,  
7 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl cyclohexene-4-  
8 methylene radical, cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-  
9 ethylene radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl  
10 cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical,  
11 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-  
12 ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical, cyclohexene-  
13 4-propylene radical, 1-methyl cyclohexene-4-propylene radical, 2-methyl  
14 cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-propylene radical,  
15 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl cyclohexene-4-  
16 propylene radical, 2,5-dimethyl cyclohexene-4-propylene radical,  
17 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-methylene  
18 radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-  
19 methylene radical, 1,2-dimethyl cyclopentene-4-methylene radical,  
20 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-  
21 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical,  
22 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl  
23 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl  
24 cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical,  
25 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-  
26 ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl  
27 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene  
28 radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-  
29 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl  
30 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene  
31 radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl  
32 cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene

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- 1 radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and  
2 1,2,3,5-tetramethyl cyclopentene-4-propylene radical.

A 3 In yet another preferred embodiment of the invention, the <sup>Compound</sup> composition of the  
4 above compositions, article, layer and process is a ethylene/methyl  
5 acrylate/cyclohexenyl methyl acrylate terpolymer, a cyclohexenyl methyl  
6 acrylate/ethylene copolymer, a cyclohexenyl methyl methacrylate/styrene  
7 copolymer, a cyclohexenyl methyl acrylate homopolymer or a methyl  
8 acrylate/cyclohexenyl methyl acrylate copolymer.

9 In another preferred embodiment of the invention, the odor and taste  
10 characteristics of products packaged with material comprised of the above  
11 <sup>Compound</sup> compositions, article, layer and process are not adulterated as a result of  
12 oxidation of the composition.

13 In still another preferred embodiment of the invention, there is no significant  
14 fragmentation of the olefinic pendent groups and linking groups from the  
15 polymeric backbone as a result of oxidation of the above <sup>Compound</sup> compositions, article,  
16 layer and process.

A 17 In yet another preferred embodiment of the invention, the transition metal  
18 catalyst of the above oxygen scavenging <sup>Compound</sup> composition, article of manufacture,  
19 layer and process is a metal salt.

Co salt 20 In still another preferred embodiment of the invention, the metal in the metal  
21 salt of the above oxygen scavenging <sup>Compound</sup> composition, article of manufacture,  
22 layer and process is cobalt.

A 23 In still another preferred embodiment of the invention, the metal salt of the  
24 above oxygen scavenging <sup>Compound</sup> composition, article of manufacture, layer and  
25 process is selected from the group consisting of cobalt neodecanoate, cobalt  
26 2-ethylhexanoate, cobalt oleate and cobalt stearate.

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A 1 In yet another preferred embodiment of the invention, the composition of the  
2 above oxygen scavenging <sup>composition</sup> composition, article of manufacture, layer and  
3 process further comprises at least one triggering material to enhance initiation  
4 of oxygen scavenging.

5 In still another preferred embodiment of the invention, the triggering material  
6 of the above oxygen scavenging composition, article of manufacture, layer  
7 and process is a photo initiator.

8 In a preferred embodiment of the invention, the above article of manufacture  
9 is a package.

10 In another preferred embodiment of invention, the package article of the  
11 above article of manufacture comprises a flexible film having a thickness of at  
12 most 10 mil or a flexible sheet having a thickness of at least 10 mil.

13 In yet another preferred embodiment of the invention, the oxygen scavenging  
14 system of the package article of the above article of manufacture comprises at  
15 least one additional layer selected from among oxygen barrier layers,  
16 polymeric selective layers, and heat seal layers.

17 In still another preferred embodiment of the invention, the above article of  
18 manufacture is a package with a food product located within the package.

19 In yet another preferred embodiment of the invention, the above article of  
20 manufacture is a package for packaging a cosmetic, chemical, electronic  
21 device, pesticide or a pharmaceutical composition.

22 In still another preferred embodiment of the invention, a multi-layer film  
23 comprises the article of the above article of manufacture and the film has at  
24 least one additional functional layer.

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1 In yet another preferred embodiment of the invention, the multi-layer film of  
2 the above article of manufacture has at least one additional layer selected  
3 from among oxygen barrier layers, polymeric selective barrier layers,  
4 structural layers and heat seal layers.

5 In still another preferred embodiment of the invention, the multi-layer film of  
6 the above article of manufacture has at least one additional layer which is an  
7 oxygen barrier layer.

8 In yet another preferred embodiment of the invention, the multi-layer film of  
9 the above article of manufacture further comprises at least one polymeric  
10 selective barrier layer.

✓ 11 In still another preferred embodiment of the invention, the multi-layer film of  
12 the above article of manufacture further comprises at least one heat seal  
13 layer.

14 In yet another preferred embodiment of the invention, the multi-layer film of  
15 the above article of manufacture further comprises at least one structural  
16 layer.

17 In still another preferred embodiment of the invention, the above article of  
18 manufacture is a rigid container, sealing gasket, patch, container closure  
19 device, bottle cap, bottle cap insert or molded or thermoformed shape.

20 In yet another preferred embodiment of the invention, the molded or  
21 thermoformed shape of the above article of manufacture is a bottle or tray.

22 In still another preferred embodiment of the invention, the above layer in  
23 addition comprises polymeric diluent.

✓ 24 In yet another preferred embodiment of the invention, the diluent of the above  
25 layer is a thermoplastic polymer.

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1 In still another preferred embodiment of the invention, the above layer is  
2 adjacent to one or more additional layers.

3 In still another preferred embodiment of the invention, at least one of the  
4 additional layers adjacent to the above layer is an oxygen barrier.

5 In still another preferred embodiment of the invention, the oxygen barrier of  
6 the above layer comprises a member of the group consisting of poly(ethylene-  
7 vinyl alcohol), polyacrylonitrile, poly(vinyl chloride), polyamides,  
8 poly(vinylidene dichloride), poly(ethylene terephthalate), silica, metal foil and  
9 metalized polymeric films.

10 In still another preferred embodiment of the invention, the one or more of said  
11 additional layer or layers of the above layer is coextruded with the above  
12 layer.

13 In yet another preferred embodiment of the invention, the one or more of said  
14 additional layer or layers of the above layer is laminated onto the above layer.

15 In still another preferred embodiment of the invention, the one or more of said  
16 additional layer or layers of the above layer is coated onto the above layer.

17 In yet another preferred embodiment of the invention, the above layer is  
18 flexible.

19 In still another preferred embodiment of the invention, the above layer is  
20 transparent.

21 In yet another preferred embodiment of the invention, an article for packaging  
22 wherein the article comprises the above layer.

23 In yet another preferred embodiment of the invention, the above process of  
24 making the oxygen scavenging packaging material comprises the steps of:

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- 1 (a) selecting polymers from the group consisting of styrene/maleic  
2 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,  
3 ethylene/methacrylic acid, acrylic acid, methacrylic acid,  
4 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl  
5 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate,  
6 and styrene/methyl methacrylate to form a mixture and combining the  
7 polymers with an esterifying/transesterifying compound selected from  
8 the group consisting of cyclohexene-4-methanol, 1-methyl cyclohexene-  
9 4-methanol, 2-methyl cyclohexene-4-methanol, 5-methyl cyclohexene-4-  
10 methanol, 1,2-dimethyl cyclohexene-4-methanol, 1,5-dimethyl  
11 cyclohexene-4-methanol, 2,5-dimethyl cyclohexene-4-methanol,  
12 1,2,5-trimethyl cyclohexene-4-methanol, cyclohexene-4-ethanol,  
13 1-methyl cyclohexene-4-ethanol, 2-methyl cyclohexene-4-ethanol,  
14 5-methyl cyclohexene-4-ethanol, 1,2-dimethyl cyclohexene-4-ethanol,  
15 1,5-dimethyl cyclohexene-4-ethanol, 2,5-dimethyl cyclohexene-4-  
16 ethanol, 1,2,5-trimethyl cyclohexene-4-ethanol, cyclohexene-4-propanol,  
17 1-methyl cyclohexene-4-propanol, 2-methyl cyclohexene-4-propanol,  
18 5-methyl cyclohexene-4-propanol, 1,2-dimethyl cyclohexene-4-propanol,  
19 1,5-dimethyl cyclohexene-4-propanol, 2,5-dimethyl cyclohexene-4-  
20 propanol, 1,2,5-trimethyl cyclohexene-4-propanol, cyclopentene-4-  
21 methanol, 1-methyl cyclopentene-4-methanol, 3-methyl cyclopentene-4-  
22 methanol, 1,2-dimethyl cyclopentene-4-methanol, 3,5-dimethyl  
23 cyclopentene-4-methanol, 1,3-dimethyl cyclopentene-4-methanol,  
24 2,3-dimethyl cyclopentene-4-methanol, 1,2,3-trimethyl cyclopentene-4-  
25 methanol, 1,2,3,5-tetramethyl cyclopentene-4-methanol, cyclopentene-4-  
26 ethanol, 1-methyl cyclopentene-4-ethanol, 3-methyl cyclopentene-4-  
27 ethanol, 1,2-dimethyl cyclopentene-4-ethanol, 3,5-dimethyl  
28 cyclopentene-4-ethanol, 1,3-dimethyl cyclopentene-4-ethanol,  
29 2,3-dimethyl cyclopentene-4-ethanol, 1,2,3-trimethyl cyclopentene-4-  
30 ethanol, 1,2,3,5-tetramethyl cyclopentene-4-ethanol, cyclopentene-4-  
31 propanol, 1-methyl cyclopentene-4-propanol, 3-methyl cyclopentene-4-  
32 propanol, 1,2-dimethyl cyclopentene-4-propanol, 3,5-dimethyl

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- 1 cyclopentene-4-propanol, 1,3-dimethyl cyclopentene-4-propanol,  
2 2,3-dimethyl cyclopentene-4-propanol, 1,2,3-trimethyl cyclopentene-4-  
3 propanol, and 1,2,3,5-tetramethyl cyclopentene-4-propanol;
- 4 (b) heating the polymers and esterifying/transesterifying compounds  
5 selected in (a) to form a polymer melt;
- 6 (c) processing the melt in an extruder under esterification/transesterification  
7 conditions with esterification/transesterification catalysts and  
8 antioxidants protecting the melt from oxidation during extrusion, so that  
9 the polymer melt undergoes esterification of polymeric anhydrides with  
10 cyclic olefin pendent groups, esterification of polymeric acids with cyclic  
11 olefin pendent groups or exchange of alkyl groups of polymeric esters  
12 with cyclic olefin pendent groups; and
- 13 (d) removing volatile organic products and by-products from the melt.
- 14 In still another preferred embodiment of the invention, the above process of  
15 making the oxygen scavenging packaging material comprises the steps of:
- 16 (a) selecting polymers from the group consisting of styrene/maleic  
17 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,  
18 ethylene/methacrylic acid, acrylic acid, methacrylic acid,  
19 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl  
20 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate,  
21 and styrene/methyl methacrylate to form a mixture and combining the  
22 polymers with an amidizing/transamidizing compound selected from the  
23 group consisting of cyclohexene-4-methyl amine, 1-methyl cyclohexene-  
24 4-methyl amine, 2-methyl cyclohexene-4-methyl amine, 5-methyl  
25 cyclohexene-4-methyl amine, 1,2-dimethyl cyclohexene-4-methyl amine,  
26 1,5-dimethyl cyclohexene-4-methyl amine, 2,5-dimethyl cyclohexene-4-  
27 methyl amine, 1,2,5-trimethyl cyclohexene-4-methyl amine,

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- 1 cyclohexene-4-ethyl amine, 1-methyl cyclohexene-4-ethyl amine,  
2 2-methyl cyclohexene-4-ethyl amine, 5-methyl cyclohexene-4-ethyl  
3 amine, 1,2-dimethyl cyclohexene-4-ethyl amine, 1,5-dimethyl  
4 cyclohexene-4-ethyl amine, 2,5-dimethyl cyclohexene-4-ethyl amine,  
5 1,2,5-trimethyl cyclohexene-4-ethyl amine, cyclohexene-4-propyl amine,  
6 1-methyl cyclohexene-4-propyl amine, 2-methyl cyclohexene-4-propyl  
7 amine, 5-methyl cyclohexene-4-propyl amine, 1,2-dimethyl cyclohexene-  
8 4-propyl amine, 1,5-dimethyl cyclohexene-4-propyl amine, 2,5-dimethyl  
9 cyclohexene-4-propyl amine, 1,2,5-trimethyl cyclohexene-4-propyl  
10 amine, cyclopentene-4-methyl amine, 1-methyl cyclopentene-4-methyl  
11 amine, 3-methyl cyclopentene-4-methyl amine, 1,2-dimethyl  
12 cyclopentene-4-methyl amine, 3,5-dimethyl cyclopentene-4-methyl  
13 amine, 1,3-dimethyl cyclopentene-4-methyl amine, 2,3-dimethyl  
14 cyclopentene-4-methyl amine, 1,2,3-trimethyl cyclopentene-4-methyl  
15 amine, 1,2,3,5-tetramethyl cyclopentene-4-methyl amine, cyclopentene-  
16 4-ethyl amine, 1-methyl cyclopentene-4-ethyl amine, 3-methyl  
17 cyclopentene-4-ethyl amine, 1,2-dimethyl cyclopentene-4-ethyl amine,  
18 3,5-dimethyl cyclopentene-4-ethyl amine, 1,3-dimethyl cyclopentene-4-  
19 ethyl amine, 2,3-dimethyl cyclopentene-4-ethyl amine, 1,2,3-trimethyl  
20 cyclopentene-4-ethyl amine, 1,2,3,5-tetramethyl cyclopentene-4-ethyl  
21 amine, cyclopentene-4-propyl amine, 1-methyl cyclopentene-4-propyl  
22 amine, 3-methyl cyclopentene-4-propyl amine, 1,2-dimethyl  
23 cyclopentene-4-propyl amine, 3,5-dimethyl cyclopentene-4-propyl  
24 amine, 1,3-dimethyl cyclopentene-4-propyl amine, 2,3-dimethyl  
25 cyclopentene-4-propyl amine, 1,2,3-trimethyl cyclopentene-4-propyl  
26 amine, and 1,2,3,5-tetramethyl cyclopentene-4-propyl amine;
- 27 (b) heating the polymers and amidizing/transamidizing compounds selected  
28 in (a) to form a polymer melt;
- 29 (c) processing the melt in an extruder under amidation/transamidation  
30 conditions with amidation/transamidation catalysts and antioxidants

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1 protecting the melt from oxidation during extrusion, so that the polymer  
2 melt undergoes amidation of polymeric anhydrides with cyclic olefin  
3 pendent groups, amidation of polymeric acids with cyclic olefin pendent  
4 groups or exchange of alkyl groups of polymeric esters with cyclic olefin  
5 pendent groups; and

6 (d) removing volatile organic products and by-products from the melt.

7 In yet another preferred embodiment of the invention, the above process of  
8 making of the oxygen scavenging packaging material comprises the steps of:

9 (a) adding to an autoclave, ethylene and a vinyl monomer comprising a  
10 pendent cyclohexene;

11 (b) stirring the ethylene and the vinyl monomer in the autoclave to achieve a  
12 mixture;

13 (c) adding a polymerization initiator before, during or after the stirring step;

14 (d) polymerizing the mixture to achieve a polymer; and

15 (e) isolating and purifying the polymer.

16 In still another embodiment of the invention, in the above process, in step (a),  
17 an alpha-olefin is added to the autoclave along with the ethylene and the vinyl  
18 monomer and, in step (b), the alpha-olefin is stirred with the ethylene and the  
19 vinyl monomer to achieve the mixture.

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DESCRIPTION OF THE DRAWINGS

- 1
- 2 Figure 1 is a schematic showing the overall process leading to the
- 3 transesterification of ethylene methyl acrylate copolymers (EMAC) to give
- 4 modified EMAC having cyclic pendent olefins.
- 5 Figure 2 is a graph comparatively plotting percent oxygen in headspace at
- 6 4°C (initially at 1% oxygen) against time in days for two 3-layer film extrusions
- 7 based on Dowlex® 3010/EMCM/Dowlex® 3010 films (EMCM being an
- 8 acronym for ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer
- 9 also referred to as poly(ethylene/methyl acrylate/cyclohexene-methyl
- 10 acrylate)), both including the EMCM inner layer and one of them having
- 11 50 ppm of a non-volatile antioxidant Irganox® 1010 in the EMCM layer and
- 12 one of them having 100 ppm Irganox® 1010 in the EMCM layer.
- 13 Figure 3 is a graph comparatively plotting percent oxygen in headspace at
- 14 4°C (initially at 1% oxygen) against time in days for an EMCM film and two
- 15 EBAC blended EMCM films, one of them having 3:1 EBAC:EMCM and one of
- 16 them having 1:1 EBAC:EMCM.
- 17 Figure 4 is a graph comparatively plotting the oxygen scavenging rates and
- 18 capacities at 25°C in which the initial headspace oxygen was 21% (air) for an
- 19 EMCM film and a 2:1 EBAC:EMCM film.
- 20 Figure 5 is a graph showing the taste ratings in a comparative taste test
- 21 between food stored in two oxygen scavenging packages (EMCM and SBS)
- 22 and a control package (no oxygen scavenger).

DETAILED DESCRIPTION OF THE INVENTION

- 23
- 24 This invention relates to an oxygen scavenging polymer <sup>compound</sup> composition
- 25 comprising <sup>cyclic olefinic</sup> cyclic allylic pendent groups which can be used in oxygen

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AA  
emcm

1 scavenging packaging material which have either no or low volatile oxidation  
2 by-products. Minimizing volatile by-products reduces the problem of  
3 organoleptics in oxygen scavenging food packaging.

4 The polymer <sup>Compound cyclic olefinic</sup> composition with cyclic allylic pendent groups can be made by  
5 grafting methyl cyclohex-1-ene-4-methanol, cyclohex-1-ene-4-methanol  
6 (1,2,5,6-tetrahydrobenzyl alcohol) and cyclohex-1-ene-4-propanol onto EMAC  
7 resins by transesterification of the corresponding alcohols or transamidation of  
8 the corresponding amines with the methyl esters on EMAC to give modified  
9 EMAC having pendent cyclic olefins (see Figure 1). The <sup>Compound</sup> composition can also  
10 be made by direct polymerization.

11 The esterification, transesterification, amidation or transamidation reaction  
12 can be a solution reaction or by reactive extrusion. The catalysts can be any  
13 one of strong non-oxidizing acids, tertiary amines, Group I alkoxides,  
14 Group IVB alkoxides and Group IVA metal organics. The level of olefin in the  
15 final products can be controlled by the level of transesterification and the  
16 methyl ester content of the start EMAC. The molecular weight of the  
17 polymers largely depends on the molecular weight of the EMAC feeds.

18 In a preferred embodiment, these products are combined with a transition-  
19 metal salt to catalyze the oxygen scavenging properties of the materials. A  
20 transition-metal salt, as the term is used here, comprises an element chosen  
21 from the first, second and third transition series of the periodic table of the  
22 elements, particularly one that is capable of promoting oxidation reactions.  
23 This transition-metal salt is in a form which facilitates or imparts scavenging of  
24 oxygen by the composition of this invention. A plausible mechanism, not  
25 intended to place limitations on this invention, is that the transition element  
26 can readily inter-convert between at least two oxidation states and facilitates  
27 formation of free radicals. Suitable transition-metal elements include, but are  
28 not limited to, manganese II or III, iron II or III, cobalt II or III, nickel II or III,  
29 copper I or II, rhodium II, III or IV, and ruthenium. The oxidation state of the

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1 transition-metal element when introduced into the composition is not  
2 necessarily that of the active form. It is only necessary to have the transition-  
3 metal element in its active form at or shortly before the time that the  
4 composition is required to scavenge oxygen. The transition-metal element is  
5 preferably iron, nickel or copper, more preferably manganese and most  
6 preferably cobalt.

7 Suitable counter-ions for the transition metal element are organic or inorganic  
8 anions. These include, but are not limited to, chloride, acetate, stearate,  
9 oleate, palmitate, 2-ethylhexanoate, citrate, glycolate, benzoate,  
10 neodecanoate or naphthenate. Organic anions are preferred. Particularly  
11 preferable salts include cobalt 2-ethylhexanoate, cobalt benzoate, cobalt  
12 stearate, cobalt oleate and cobalt neodecanoate. The transition-metal  
13 element may also be introduced as an ionomer, in which case a polymeric  
14 counter-ion is employed.

15 The composition of the present invention when used in forming a oxygen  
16 scavenging packaging article can be composed solely of the above described  
17 polymer and transition metal catalyst. However, components, such as  
18 photoinitiators, can be added to further facilitate and control the initiation of  
19 oxygen scavenging properties. For instance, it is often preferable to add a  
20 photoinitiator, or a blend of different photoinitiators, to the oxygen scavenger  
21 compositions, especially when antioxidants are included to prevent premature  
22 oxidation of that composition during processing.

23 Suitable photoinitiators are well known in the art. Such photoinitiators are  
24 discussed in U.S. Patent No. 5,211,875. It is also discussed in U.S. Patent  
25 Application Serial No. 08/857,325, in which some of the present inventors  
26 were contributing inventors and which is incorporated herein by reference.  
27 Specific examples include, but are not limited to, benzophenone, o-methoxy-  
28 benzophenone, acetophenone, o-methoxy-acetophenone,  
29 acenaphthenequinone, methyl ethyl ketone, valerophenone, hexanophenone,

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1  $\alpha$ -phenyl-butyrophenone, p-morpholinopropiophenone, dibenzosuberone,  
2 4-morpholinobenzophenone, benzoin, benzoin methyl ether,  
3 4-o-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone,  
4 4'-methoxyacetophenone, substituted and unsubstituted anthraquinones,  
5  $\alpha$ -tetralone, 9-acetylphenanthrene, 2-acetyl-phenanthrene,  
6 10-thioxanthenone, 3-acetyl-phenanthrene, 3-acetylindole, 9-fluorenone,  
7 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one,  
8 7-H-benz[de]anthracen-7-one, benzoin tetrahydropyranyl ether,  
9 4,4'-bis(dimethylamino)-benzophenone, 1'-acetonaphthone,  
10 2'-acetonaphthone, acetonaphthone and 2,3-butanedione,  
11 benz[a]anthracene-7,12-dione, 2,2-dimethoxy-2-phenylacetophenone,  
12  $\alpha,\alpha$ -diethoxy-acetophenone,  $\alpha,\alpha$ -dibutoxyacetophenone, etc. Singlet oxygen  
13 generating photosensitizers such as Rose Bengal, methylene blue, and  
14 tetraphenyl porphine may also be employed as photoinitiators. Polymeric  
15 initiators include polyethylene carbon monoxide and oligo[2-hydroxy-2-methyl-  
16 1-[4-(1-methylvinyl)phenyl]propanone]. Use of a photoinitiator is preferable  
17 because it generally provides faster and more efficient initiation.

18 When a photoinitiator is used, its primary function is to enhance and facilitate  
19 the initiation of oxygen scavenging upon exposure to radiation. The amount  
20 of photoinitiator can vary. In many instances, the amount will depend on the  
21 amount and type of oxygen scavenging polymer in the present invention, the  
22 wavelength and intensity of radiation used, the nature and amount of  
23 antioxidants used, as well as the type of photoinitiator used. The amount of  
24 photoinitiator also depends on how the scavenging composition is used. For  
25 instance, if the photoinitiator-coating composition is placed underneath a layer  
26 which is somewhat opaque to the radiation used, more initiator may be  
27 needed. For most purposes, however, the amount of photoinitiator, when  
28 used, will be in the range of 0.01 to 10% by weight of the total composition.  
29 The initiating of oxygen scavenging can be accomplished by exposing the  
30 packaging article to actinic or electron beam radiation, as described below.

1 Antioxidants may be incorporated into the scavenging compositions of this  
2 invention to control degradation of the components during compounding and  
3 shaping. An antioxidant, as defined herein, is any material which inhibits  
4 oxidative degradation or cross-linking of polymers. Typically, such  
5 antioxidants are added to facilitate the processing of polymeric materials  
6 and/or prolong their useful shelf-life.

7 Antioxidants such as Vitamin E, Irganox® 1010, Irganox® 1076,  
8 2,6-di(t-butyl)-4-methyl-phenol(BHT), 2,6-di(t-butyl)-4-ethyl-phenol (BHEB),  
9 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite,  
10 tris-(nonylphenyl)phosphite and dilaurylthiodipropionate would be suitable for  
11 use with this invention.

12 When an antioxidant is included as part of the present composition, it should  
13 be used in amounts which will prevent oxidation of the scavenger  
14 composition's components as well as other materials present in a resultant  
15 blend during formation and processing but the amount should be less than  
16 that which would interfere with the scavenging activity of the resultant layer,  
17 film or article. The particular amount needed will depend on the particular  
18 components of the composition, the particular antioxidant used, the degree  
19 and amount of thermal processing used to form the shaped article, and the  
20 dosage and wavelength of radiation applied to initiate oxygen scavenging and  
21 can be determined by conventional means. Typically, they are present in  
22 about 0.01 to 1% by weight.

23 Other additives which may also be included in oxygen scavenger layers  
24 include, but are not necessarily limited to, fillers, pigments, dyestuffs,  
25 stabilizers, processing aids, plasticizers, fire retardants, anti-fog agents, etc.

26 The amounts of the components which are used in the oxygen scavenging  
27 compositions, or layers have an effect on the use, effectiveness and results of  
28 this method. Thus, the amounts of polymer, transition metal catalyst and any

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*Antioxidants*

1 photoinitiator, antioxidant, polymeric diluents and additives, can vary  
2 depending on the article and its end use.

3 For instance, one of the primary functions of the polymer described above is  
4 to react irreversibly with oxygen during the scavenging process, while the  
5 primary function of the transition metal catalyst is to facilitate this process.

6 Thus, to a large extent, the amount of polymer present will affect the oxygen  
7 scavenging capacity of the composition, i.e., affect the amount of oxygen that  
8 the composition can consume. The amount of transition metal catalyst will  
9 affect the rate at which oxygen is consumed. Because it primarily affects the  
10 scavenging rate, the amount of transition metal catalyst may also affect the  
11 onset of oxygen scavenging (induction period).

12 It has been found that the subject polymers, when used as part of the present  
13 composition, provide oxygen scavenger properties at desirable rate and  
14 capacity while causing the composition to have enhanced processability and  
15 compatibility properties over conventional ethylenically unsaturated polymers.  
16 Thus, the present composition can be used to provide, by itself or as a blend  
17 with diluent polymers, such as polyolefins and the like, a packaging material  
18 or film having enhanced processability properties. Further, the present  
19 composition consumes and depletes the oxygen within a package cavity  
20 without substantially detracting from the color, taste and/or odor of the product  
21 contained within the package cavity.

22 The amount of the above-described polymer contained as part of the present  
23 composition may range from about 1 to 100% by weight of the composition or  
24 layer composed of said composition in which both polymer and transition  
25 metal catalyst are present (hereinafter referred to as the "scavenging  
26 composition", e.g., in a coextruded film or container, the scavenging  
27 composition would comprise the particular layer(s) in which both the  
28 copolymer and transition metal catalyst components are present together).  
29 Typically, the amount of transition metal catalyst may range from 0.001 to 1%

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1 (10 to 10,000 ppm) of the scavenging composition, based on the metal  
2 content only (excluding ligands, counterions, etc.). In the event the amount of  
3 transition metal catalyst is less than 1%, it follows that the polymer and any  
4 additives will comprise substantially all of the remainder of the composition.  
5 The polymer of the present invention may further be combined with other  
6 polymeric oxygen scavenger agents.

7 Any further additives employed normally will not comprise more than 10% of  
8 the scavenging composition, with preferable amounts being less than 5% by  
9 weight of the scavenging composition.

10 Optionally, the compositions and process of this invention can include  
11 exposure of the polymer containing the oxygen scavenging-promoting  
12 transition metal to actinic radiation to reduce the induction period, if any,  
13 before oxygen scavenging commences. A method is known for initiating  
14 oxygen scavenging by exposing a film comprising an oxidizable organic  
15 compound and a transition metal catalyst to actinic radiation. A composition  
16 of the present invention which has a long induction period in the absence of  
17 actinic radiation but a short or non-existent induction period after exposure to  
18 actinic radiation is particularly preferred. They maintain a high capability for  
19 scavenging oxygen upon activation with actinic radiation. Thus, oxygen  
20 scavenging can be activated when desired.

21 The radiation used in this method should be actinic, e.g., ultraviolet or visible  
22 light having a wavelength of about 200 to 750 nanometers (nm), and  
23 preferably having a wavelength of about 200 to 600 nm, and most preferably  
24 from about 200 to 400 nm. When employing this method, it is preferable to  
25 expose the oxygen scavenger to at least 0.01 Joule per gram of scavenging  
26 composition. A typical amount of exposure is in the range of 10 to  
27 2000 Joules per gram. The radiation can also be an electron beam radiation  
28 at a dosage of about 2 to 200 kiloGray, preferably about 10 to 100 kiloGray.  
29 Other sources of radiation include ionizing radiation such as gamma, X-rays

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1 and corona discharge. The duration of exposure depends on several factors  
2 including, but not limited to, the amount and type of photoinitiator present,  
3 thickness of the layers to be exposed, thickness and opacity of intervening  
4 layers amount of any antioxidant present, and the wavelength and intensity of  
5 the radiation source. The radiation provided by heating of polyolefin and the  
6 like polymers (e.g., 100-250°C) during processing does not cause triggering.

7 Oxygen-scavenging compositions of the present invention are useful in many  
8 ways. The compositions can be dispersed as small particles for absorbing  
9 oxygen or can be coated onto materials such as metallic foil, polymer film,  
10 metalized film, paper or cardboard to provide, in some embodiments,  
11 scavenging properties and/or adhesive properties. The compositions are also  
12 useful in making articles such as single or multi-layer rigid thick-walled plastic  
13 containers or bottles (typically, between 5 and 100 mils in thickness) or in  
14 making single or multi-layer flexible films, especially thin films (less than  
15 5 mils, or even as thin as about 0.25 mil). Some of the compositions of the  
16 present invention are easily formed into films using well-known means. These  
17 films can be used alone or in combination with other films or materials.

18 The compositions of the present invention may be further combined with one  
19 or more polymers, such as thermoplastic polymers which are typically used to  
20 form film layers in plastic packaging articles. In the manufacture of certain  
21 packaging articles, well-known thermosets can also be used as a polymeric  
22 diluent.

23 Selecting combinations of a diluent and the composition of the present  
24 invention depends on the properties desired. Polymers which can be used as  
25 the diluent include, but are not limited to, polyethylene, low or very low density  
26 polyethylene, polypropylene, polyvinyl chloride, and ethylene copolymers  
27 such as ethylene-vinyl acetate, ethylene-alkyl acrylates or methacrylates,  
28 ethylene-acrylic acid or methacrylic acid, and ethylene-arylic or metharylic  
29 acid ionomers. In rigid packaging applications, polystyrene is often used.

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1 Blends of different diluents may also be used. However, as indicated above,  
2 the selection of the polymeric diluent largely depends on the article to be  
3 manufactured and the end use. Such selection factors are well known in the  
4 art.

5 If a diluent polymer such as a thermoplastic is employed, it should further be  
6 selected according to its compatibility with the composition of the present  
7 invention. In some instances, the clarity, cleanliness, effectiveness as an  
8 oxygen-scavenger, barrier properties, mechanical properties and/or texture of  
9 the article can be adversely affected by a blend containing a polymer which is  
10 incompatible with the composition of the present invention.

11 A blend of a composition of the present invention with a compatible polymer  
12 can be made by dry blending or by melt-blending the polymers together at a  
13 temperature in the approximate range of 50°C to 250°C. Alternative methods  
14 of blending include the use of a solvent followed by evaporation. When  
15 making film layers or articles from oxygen-scavenging compositions, extrusion  
16 or coextrusion, solvent casting, injection molding, stretch blow molding,  
17 orientation, thermoforming, extrusion coating, coating and curing, lamination  
18 or combinations thereof would typically follow the blending.

19 Layers comprising the composition of the present invention may be in several  
20 forms. They may be in the form of stock films, including "oriented" or "heat  
21 shrinkable" films, which may ultimately be processed as bags, etc., or in the  
22 form of stretch-wrap films. The layers may also be in the form of sheet inserts  
23 to be placed in a packaging cavity. In rigid articles such as beverage  
24 containers, thermoformed trays or cups, the layer may be within the  
25 container's walls. Even further, the layer may also be in the form of a liner  
26 placed with or in the container's lid or cap. The layer may even be coated or  
27 laminated onto any one of the articles mentioned above.

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1 In multi-layered articles, the scavenging layer comprising the composition of  
2 the present invention may be included with layers such as, but not necessarily  
3 limited to, "oxygen barriers", i.e., layers of material having an oxygen  
4 transmission rate equal to or less than 100 cubic centimeters-mil per square  
5 meter (cc-mil/m<sup>2</sup>) per day per atmosphere pressure at room temperature, i.e.,  
6 about 25°C. Typical oxygen barriers comprise poly(ethylene vinyl alcohol),  
7 polyacrylonitrile, polyvinyl chloride, poly(vinylidene dichloride), polyethylene  
8 terephthalate, silica and polyamides. Metal foil layers can also be employed.

9 Other additional layers may include one or more layers which are permeable  
10 to oxygen. In one preferred packaging construction, especially for flexible  
11 packaging for food, the layers include, in order starting from the outside of the  
12 package to the innermost layer of the package, (i) an oxygen barrier layer,  
13 (ii) a scavenging layer, i.e., the scavenging composition as defined earlier,  
14 and, optionally, (iii) an oxygen permeable layer. Control of the oxygen barrier  
15 property of (i) allows a means to regulate the scavenging life of the package  
16 by limiting the rate of oxygen entry to the scavenging composition (ii), and  
17 thus limiting the rate of consumption of scavenging capacity. Control of the  
18 oxygen permeability of layer (iii) allows a means to set an upper limit on the  
19 rate of oxygen scavenging for the overall structure independent of the  
20 composition of the scavenging composition (ii). This can serve the purpose of  
21 extending the handling lifetime of the films in the presence of air prior to  
22 sealing of the package. Furthermore, layer (iii) can provide a barrier to  
23 migration of the individual components in the scavenging films or by-products  
24 of scavenging into the package interior. Even further, layer (iii) also improves  
25 the heat-sealability, clarity and/or resistance to blocking of the multi-layer film.

26 Further, additional layers such as adhesive layers may also be used.  
27 Compositions typically used for adhesive layers include anhydride functional  
28 polyolefins and other well-known adhesive layers.

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1 To determine the oxygen scavenging capabilities of a composition, the rate of  
2 oxygen scavenging can be calculated by measuring the time that elapsed  
3 before the article depletes a certain amount of oxygen from a sealed  
4 container. For instance, a film comprising the scavenging component can be  
5 placed in an air-tight, sealed container of a certain oxygen containing  
6 atmosphere, e.g., air which typically contains 20.9% oxygen by volume.  
7 Then, over a period of time, samples of the atmosphere inside the container  
8 are removed to determine the percentage of oxygen remaining. The  
9 scavenging rates of the composition and layers of the present invention will  
10 change with changing temperature and atmospheric conditions.

11 When an active oxygen barrier is prepared, the scavenging rate can be as low  
12 as 0.1 cc oxygen per gram of composition of the present invention per day in  
13 air at 25°C and a 1 atmosphere pressure. However, preferable compositions  
14 of this invention have rates equal to or greater than 1 cc oxygen per gram per  
15 day, thus making them suitable for scavenging oxygen from within a package,  
16 as well as suitable for active oxygen barrier applications. Many compositions  
17 are even capable of more preferable rates equal to or greater than 5.0 cc O<sub>2</sub>  
18 per gram per day.

19 Generally, film layers suitable for use as an active oxygen barrier can have an  
20 oxygen transmission rate as high as 10 cc oxygen per square meter per mil  
21 per day when measured in air at 25°C and 1 atmosphere pressure.  
22 Preferably, a layer of this invention has an oxygen transmission rate less than  
23 about 1 cc oxygen per square meter per mil per day, and more preferably has  
24 an oxygen transmission rate less than about 0.2 cc oxygen per square meter  
25 per rail per day under the same conditions, thus making it suitable for active  
26 oxygen barrier applications as well as for scavenging oxygen from within a  
27 package.

28 In an active oxygen barrier application, it is preferable that the combination of  
29 oxygen barriers and any oxygen scavenging activity create an overall oxygen

1 transmission rate of less than about 1.0 cubic centimeter-mil per square meter  
2 per day per atmosphere pressure at 25°C. Another definition of acceptable  
3 oxygen scavenging is derived from testing actual packages. In actual use, the  
4 scavenging rate requirement will largely depend on the internal atmosphere of  
5 the package, the contents of the package and the temperature at which it is  
6 stored.

7 In a packaging article made according to this invention, the scavenging rate  
8 will depend primarily on the amount and nature of the composition of the  
9 present invention in the article, and secondarily on the amount and nature of  
10 other additives (e.g., diluent polymer, antioxidant, etc.) which are present in  
11 the scavenging component, as well as the overall manner in which the  
12 package is fabricated, e.g., surface area/volume ratio.

13 The oxygen scavenging capacity of an article comprising the invention can be  
14 measured by determining the amount of oxygen consumed until the article  
15 becomes ineffective as a scavenger. The scavenging capacity of the package  
16 will depend primarily on the amount and nature of the scavenging moieties  
17 present in the article, as discussed above.

18 In actual use, the oxygen scavenging capacity requirement of the article will  
19 largely depend on three parameters of each application:

- 20 (1) the quantity of oxygen initially present in the package;
- 21 (2) the rate of oxygen entry into the package in the absence of the  
22 scavenging property; and
- 23 (3) the intended shelf life for the package.

24 The scavenging capacity of the composition can be as low as 1 cc oxygen per  
25 gram, but is preferably at least 10 cc oxygen per gram, and more preferably at

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1 least 50 cc oxygen per gram. When such compositions are in a layer, the  
2 layer will preferably have an oxygen capacity of at least 250 cc oxygen per  
3 square meter per mil thickness and more preferably at least 500 cc oxygen  
4 per square meter per mil thickness.

5 Other factors may also affect oxygen scavenging and should be considered  
6 when selecting compositions. These factors include but are not limited to  
7 temperature, relative humidity, and the atmospheric environment in the  
8 package.

9 Non-limiting examples are given in Examples 1 and 2 below of experimental  
10 conditions that were used for preparation of the polymers. Non-limiting  
11 examples of the resin preparation followed by steam stripping as well as  
12 compounding the polymers with oxidation catalyst, such as cobalt oleate and  
13 a photoinitiator, such as Methanone, [5'-(5'-(4-benzoylphenyl)[1,1':3',  
14 1"-terphenyl]-4,4"-diyl]bis[phenyl- (hereinafter referred to as BBP<sup>3</sup>), and  
15 extruded into a 3-layer film having a PE/oxygen scavenging polymer/PE  
16 structure are provided in Examples 3 through 6 below.

17 Headspace studies of three layer films made by compounding catalyst  
18 package with both fresh and aged (20 months stored in air at ambient  
19 temperature) resins after UV triggering give a very fast rate of oxygen  
20 scavenging and the resulting packages are relatively non-odorous.

21 Non-limiting examples of such studies are given in Examples 7 and 8.

22 Furthermore, the above polymer can be further diluted by a lower cost oxygen  
23 permeable resin, such as EBAC or PE or EVA, down to 50 and even 25% of  
24 the original concentration and still maintain a high oxygen scavenging rate, as  
25 the non-limiting examples in Examples 9 and 10 show.

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EXAMPLES

Example 1

Polymer Preparation (C1641-6)

550 ml of decalin® was placed in a flask. To this was added 350 g of Chevron EMAC SP-2260 which has 24 weight % of methyl acrylate (0.9767 moles of methyl acrylate) and 0.48 g of Irganox®1076 (0.1 mole). The temperature of the mixture was gradually raised while stirring. When the temperature reached approximately 120°C, 127.1 g (0.9767 moles) of 3-methyl-cyclohex-1-ene-4-methanol (97%) was added. When the temperature reached approximately 140°C, 4.8 g of the catalyst Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> was added a portion at a time. The temperature was maintained at 170°C while stirring. The course of the reaction was observed by subjecting samples of the mixture to NMR at hourly intervals. The percent conversion is given in Table 1 below. After 5 hours of reaction, the mixture was cooled and 400 ml of CHCl<sub>3</sub> was added and the mixture was then precipitated by adding it to 4 liters of CH<sub>3</sub>OH in a Waring blender. The precipitate is filtered and washed with CH<sub>3</sub>OH and dried in a vacuum oven at 50°C. The dried mixture yielded 407.5 g of ethylene/methyl acrylate/methyl cyclohexene methyl acrylate (EMCM).

Table 1

Time (hours)	Percent Conversion
1 hour	50%
2 hours	62.3%
3 hours	65.5%
5 hours	87.1%

390 grams of a combination of the above prepared polymer and the same polymer prepared under the same conditions in a different batch, which



1 together have a conversion percentage of 68.8%, was solvent coated with  
2 3.25 g cobalt-neodecanoate in 70 ml normal hexane. The mixture was tumble  
3 dried for 1.5 hours and residual solvent removed in a vacuum.

4 Example 2

5 Polymer Preparation

6 600 ml of decalin was placed in a flask. To this was added 334 grams of  
7 Chevron SP-2260 (0.9330 moles of methyl acrylate) and 0.44 g of Irganox®  
8 1010 (0.1% mole). The temperature of the mixture was gradually raised while  
9 stirring. When the temperature reached approximately 120°C, 104.6 g  
10 (0.93 moles) of cyclohex-1-ene-4-methanol was added. When the  
11 temperature reached approximately 140°C, 4.4 g of the catalyst  $Ti(OC_2H_5)_4$   
12 was added a portion at a time. The temperature was maintained at 160°C  
13 while stirring. The course of the reaction was observed by subjecting samples  
14 of the mixture to NMR at hourly intervals. The percent conversion is given in  
15 Table 2 below. After 3 hours of reaction, the mixture was cooled and 400 ml  
16 of  $CHCl_3$  was added and the mixture was then precipitated by adding it to  
17 4 liters of  $CH_3OH$  in a Waring blender. The precipitate was filtered and  
18 washed with  $CH_3OH$  and dried in a vacuum oven at 50°C. The dried mixture  
19 yielded 380.5 g of polymer.

20 Table 2

Time (hours)	Percent Conversion
1 hour	43.8%
2 hours	56.7%
3 hours	55.7%

21  
22 185 grams of the above-prepared polymer was combined with 45 ml normal  
23 hexane and 1.54 g cobalt-neodecanoate resulting in 1000 ppm of cobalt ion  
24 and 0.0185 g Irganox® 1010 resulting in 100 ppm Irganox®. The mixture was

1 heated and blended and then dried in a vacuum-oven. The resulting  
2 compound was extruded into a film.

3 Additionally, 185 grams of the above-prepared polymer was combined with  
4 45 ml normal hexane and 1.54 g cobalt-neodecanoate (resulting in 1000 ppm  
5 of cobalt ion) and 0.046 g Irganox® 1010 (resulting in 250 ppm Irganox®).  
6 The mixture is heated and blended and then dried in a vacuum-oven. The  
7 resulting compound is extruded into a film.

8 Example 3

9 EMCM Made in ZSK-30 Extruder

10 Ethylene-methyl acrylate copolymer (EMAC) was fed into a Werner &  
11 Pfleiderer ZSK-30 twin screw extruder at 6 kg/hr, and the reactants and  
12 catalysts were added to the extruder in a subsequent reaction zone. The  
13 catalyst Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> was added with the reactants at 3 mol % or at a rate of  
14 148 cc/hr. Irganox®/Toluene solution was added at 4.5 g/900 cc using a  
15 Milton Roy 29/290 mini-pump. To obtain 100 ppm of Irganox®, it must be  
16 added at 2.2 cc/min. To obtain 50 ppm of Irganox, it must be added at  
17 1.1 cc/min. Cyclohexane methyl alcohol with 1,000 ppm of an antioxidant of  
18 BHT was added via a Milton Roy dual head at 1958 cc/hr. Steam is injected  
19 into the system at 800 cc H<sub>2</sub>O/Hr at the end of the reaction zone.

20 51 lbs of EMCM product (100 ppm Irganox® 1010, 59.3% methyl alcohol  
21 (MA), 2.98 g/10 min. Melt Flow) was produced over a period of approximately  
22 2 hours.

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9876543210

Ti

✓

✓

1

Example 4

2

EMCM Made in ZSK-30

3

45 lbs of EMCM product (100 ppm Irganox®1010, 2.38 g/10 min Melt Index)

4

was extruded over a period of approximately 3 hours. A dual steam stripping

5

setup was used in which pressurized injectors at zones 4 and 11 of the

6

extruder pumped steam at 1076 cc/hr and 728 cc/hr, respectively. Both

7

injectors were Pulse 680 pumps with a pressure of at least 800 psi, except at

8

the first measured time interval when injector (No. 4) was measured at

9

500-550 psi and injector (No. 11) was measured at 500 psi.

10

Example 5

11

Co-polymerization of Styrene and 3-Cyclohexene-1-Methanol Methacrylate

12

In a 1-liter round bottom flask, 65 grams styrene (0.625 mole), 113 grams of

13

3-cyclohexene-1-methanol methacrylate (0.625 mole), 1.25 grams of Benzoyl

14

peroxide and 450 grams of toluene were mixed and degassed by freeze-thaw

15

cycles. The degassed solution was polymerized at 70-75°C for 48 hours and

16

discharged into 2 liters of methanol in a Waring Blender. The product isolated

17

was dried in a vacuum oven at 50°C for 2 hours to give 155 grams of

18

co-polymer. NMR analysis indicates it contains 48 mole % of styrene and

19

52 mole % of 3-cyclohexene-1-methanol methacrylate. Tg by DSC is 66°C.

20

Example 6

21

Oxygen Scavenging Test of Styrene/CHMA Copolymer

22

90 weight % of the above-mentioned co-polymer and 10 weight-% of a EVA

23

based Master batch containing 1 weight % of co-oleate and 1 weight % of a

24

photoinitiator (BBP<sup>3</sup>) were processed into a 8 mil thick monolayer film. A

25

100 cm<sup>2</sup> film was irradiated at both sides to receive 800 mJoules/cm<sup>2</sup> of

26

254 nm UV on each side and sealed into a foil bag containing 300 cc of 1%

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1 oxygen. The oxygen uptake was monitored up to 11 days at 4°C and at room  
2 temperature. The results are shown in Tables 3 (4°C) and 4 (room  
3 temperature).

4 Table 3

*Synthetic method not used*

Time (days)	O <sub>2</sub> Meas. Vol%	O <sub>2</sub> Meas. Vol, ml	Vol—O <sub>2</sub> Used ml	O <sub>2</sub> Uptake ml/g	O <sub>2</sub> Uptake Avg Rate cc/m <sup>2</sup> /day	Instant Rate cc/m <sup>2</sup> /day	O <sub>2</sub> Capacity cc/m <sup>2</sup> /mil
0.0	1.05	3.15	0.00	0.00	0.00	0.00	0.00
1.1	0.94	2.77	0.32	0.18	14.79	14.79	1.62
3.9	0.49	1.42	1.63	0.92	20.73	23.03	8.15
4.8	0.39	1.11	1.91	1.08	19.81	15.78	9.57
7.0	0.30	0.84	2.17	1.22	15.40	5.72	10.83
11.0	0.09	0.25	2.74	1.54	12.43	7.22	13.72

6 Table 4

Time (days)	O <sub>2</sub> Meas. Vol%	O <sub>2</sub> Meas. Vol, ml	Vol—O <sub>2</sub> Used ml	O <sub>2</sub> Uptake ml/g	O <sub>2</sub> Uptake Avg Rate cc/m <sup>2</sup> /day	Instant Rate cc/m <sup>2</sup> /day	O <sub>2</sub> Capacity cc/m <sup>2</sup> /mil
0.0	1.04	3.12	0.00	0.00	0.00	0.00	0.00
1.1	0.48	1.42	1.65	1.03	75.28	75.28	8.26
3.9	0.09	0.26	2.78	1.73	35.40	19.96	13.92
4.8	0.04	0.11	2.93	1.82	30.26	7.89	14.63
7.0	0.01	0.03	3.01	1.87	21.39	1.91	15.05
11.0	0.01	0.03	3.01	1.87	13.64	0.00	15.05

8 Example 7

9 Polymerization of 3-cyclohexene-1-methanol acrylate

10 75 grams (0.45 mole) of 3-cyclohexene-1-methanol acrylate (CHAA), 200 ml  
11 of toluene and 0.5 grams of Benzoyl peroxide were charged into a 500 ml  
12 round-bottomed flask and degassed by freeze-thaw cycles. The degassed

1 solution was polymerized at 70-75°C for 48 hours. The viscous polymer  
2 solution was worked up by precipitating in methanol solution in a Waring  
3 blender. After vacuum drying at room temperature for 3 days, the product is a  
4 rubbery clear polymer which weighs 53 grams.

6 Example 8

7 Headspace Analysis of O<sub>2</sub> Scavenging in  
8 Dowlex® 3010/EMCM/Dowlex® 3010 Films

9 Oxygen scavenging analysis was performed using a Mocon HS750 with a  
10 headspace volume of 300 cc. The sample tested was a 0.48 g three-layer  
11 film with Dowlex® 3010 film for the two outside layers and steam stripped  
12 EMCM (59% converted) for the middle layer (50 ppm Irganox® 1010). The  
13 thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging  
14 portion of the middle layer comprised 1000 ppm Cobalt salt, 1000 ppm BBP<sup>3</sup>  
15 and was exposed for 1.6 minutes to 254 nm UV at 1 inch to receive  
16 800 mJ/cm<sup>2</sup>. The oxygen scavenging was tested with 300 cc 1% O<sub>2</sub> at 4°C.  
17 The results of the tests are given below in Table 5. These results are plotted  
18 along with the results of Example 6 in Figure 2, which graphically plots %  
19 oxygen in headspace against time (days). The oxygen scavenging uptake  
20 capacity is based on the total weight of the three-layer film.

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Tegulyn  
5th floor  
methanol  
cyclohexyl methyl  
anhydride

*Dowlex / Temp / Dowlex*

Table 5

Time (days)	O <sub>2</sub> Meas. Vol%	O <sub>2</sub> Meas. Vol, ml	Vol—O <sub>2</sub> Used ml	O <sub>2</sub> Uptake ml/g	O <sub>2</sub> Uptake Avg Rate cc/m <sup>2</sup> /day	Instant Rate cc/m <sup>2</sup> /day	O <sub>2</sub> Capacity cc/m <sup>2</sup> /mil
0.0	1.04	3.12	0.00	0.00	0.00	0.00	0.00
0.8	0.74	2.18	0.89	1.84	57.93	57.93	44.25
1.9	0.46	1.33	1.70	3.54	45.85	37.36	84.85
3.0	0.29	0.83	2.18	4.54	36.87	21.87	109.08
5.8	0.14	0.39	2.60	5.42	22.46	7.41	130.08
7.8	0.09	0.25	2.74	5.71	17.67	3.51	136.95

Example 9

Headspace Analysis of O<sub>2</sub> Scavenging in  
Dowlex® 3010/EMCM/Dowlex® 3010 Films

Oxygen scavenging analysis was performed using a Mocon HS750 with a headspace volume of 300 cc. The sample tested was a 0.47 g three-layer film with Dowlex® 3010 film for the two outside layers and steam stripped EMCM for the middle layer (50 ppm Irganox 1010)). The thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer comprised 1000 ppm Cobalt salt, 1000 ppm BBP<sup>3</sup> (a photoinitiator) exposed for 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm<sup>2</sup>. The oxygen scavenging was tested with 300 cc 1% O<sub>2</sub> at 4°C. These results are plotted along with the results of Example 7 in Figure 2, which graphically plots % oxygen in headspace against time (days).

1

Example 10

2

Headspace Analysis of O<sub>2</sub> Scavenging in Dowlex® 3010/

3

EBAC:EMCM/Dowlex® 3010 Films

4 Oxygen scavenging analysis was performed using a Mocon HS750 with a  
5 headspace volume of 300 cc. The sample tested was a 0.45 g three-layer  
6 film with Dowlex® 3010 film for the two outside layers and 3:1 EBAC  
7 (ethylene/butyl acrylate copolymer):EMCM (ethylene/methyl acrylate/  
8 cyclohexenyl methyl acrylate) for the middle layer (50 ppm Irganox® 1010)).  
9 The thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging  
10 portion of the middle layer comprised 1000 ppm of Cobalt salt, 1000 ppm  
11 BBP<sup>3</sup> was exposed for 1.6 minutes to 254 nm UV at 1 inch to receive  
12 800 mJ/cm<sup>2</sup>. The oxygen scavenging was tested with 300 cc 1% O<sub>2</sub> at 4°C.  
13 These results are plotted along with the results of Example 8 in Figure 3,  
14 which graphically plots % oxygen in headspace against time (days).

15

Example 11

16

Headspace Analysis of O<sub>2</sub> Scavenging in Dowlex® 3010/

17

EBAC:EMCM/Dowlex® 3010 Films

18 Oxygen scavenging analysis was performed using a Mocon HS750 with a  
19 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer  
20 film with Dowlex® 3010 film for the two outside layers and 1:1 EBAC:EMCM  
21 for the middle layer (50 ppm Irganox®1010)). The thickness of the layers was  
22 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer  
23 comprised 1000 ppm Cobalt Oleate salt, 1000 ppm BBP<sup>3</sup> exposed for  
24 1.6 minutes at 254 nm UV at 1 inch to receive 800 mJ/cm<sup>2</sup>. The oxygen  
25 scavenging was tested with 300 cc 1% O<sub>2</sub> at 4°C. The results of the tests are  
26 given below in Table 6. These results are plotted along with the results of  
27 Example 9 in Figure 3, which graphically plots % oxygen in headspace

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1 against time (days). The oxygen scavenging uptake capacity is based on the  
2 total weight of the 3-layer film.

3 Table 6

Time (days)	Head-space O <sub>2</sub> (Vol%)	Head-space O <sub>2</sub> (Vol, ml)	Vol—O <sub>2</sub> Used (ml)	O <sub>2</sub> Uptake (ml/g)	O <sub>2</sub> Uptake Avg Rate (cc/m <sup>2</sup> ·day)	Instant Rate (cc/m <sup>2</sup> ·day)	O <sub>2</sub> Capacity cc/m <sup>2</sup>
0.0	1.09	3.27	0.00	0.00	0.00	0.00	0.00
0.8	0.74	2.18	1.03	2.20	63.00	63.00	51.63
1.8	0.50	1.45	1.73	3.68	48.52	36.18	86.43
4.8	0.17	0.48	2.67	5.8	27.73	15.51	133.45
6.1	0.12	0.34	2.81	5.98	23.17	5.60	140.45
6.9	0.10	0.28	2.86	6.09	20.84	3.40	143.20
7.9	0.08	0.22	2.92	6.21	18.46	2.62	145.90

4

5 Example 12

6 Headspace Analysis of O<sub>2</sub> Scavenging Capacity  
7 in Dowlex® 3010/EMCM/Dowlex® 3010 Films

8 Oxygen scavenging analysis was performed using a Mocon HS750 with a  
9 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer  
10 film with Dowlex® 3010 film for the two outside layers and steam stripped  
11 EMCM for the middle layer (50 ppm Irganox®1010)). The thickness of the  
12 layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle  
13 layer comprised 1000 ppm Cobalt Oleate salt, 1000 ppm BBP<sup>3</sup> exposed for  
14 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm<sup>2</sup>. The oxygen  
15 scavenging was tested with 300 cc air at room temperature. The O<sub>2</sub> uptake  
16 capacity is based on total weight of the 3-layer film. The results of the tests  
17 are given below in Table 7. These results are plotted along with the results of  
18 Example 12 in Figure 4, which graphically plots % oxygen in headspace  
19 against time (days).

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Table 7

Time (days)	Head-space O <sub>2</sub> (Vol%)	O <sub>2</sub> Vol, (ml)	Vol-O <sub>2</sub> Used (ml)	O <sub>2</sub> Uptake (ml/g)	O <sub>2</sub> Uptake Avg Rate (cc/m <sup>2</sup> ·day)	Instant Rate (cc/m <sup>2</sup> ·day)	O <sub>2</sub> Capacity (cc/m <sup>2</sup> )
0.0	20.60	61.80	0.00	0.00	0.0	0.0	0.0
1.0	13.40	39.53	21.24	43.35	1058	1058	1062
2.0	12.20	35.38	24.72	50.45	616	173	1236
3.0	11.80	33.63	25.86	52.78	437	60	1293
6.2	11.80	33.04	25.86	52.78	207	0.0	1293

Example 13

Headspace Analysis of O<sub>2</sub> Scavenging Capacity in Dowlex® 3010/EBAC:EMCM/Dowlex® 3010 Films

Oxygen scavenging analysis was performed using a Mocon HS750 with a headspace volume of 300 cc. The sample tested was a 0.45 g three-layer film with Dowlex® 3010 film for the two outside layers and 2:1 EBAC:EMCM for the middle layer (50 ppm Irganox 1010)). The width of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer comprised 1000 ppm of Cobalt salts, 1000 ppm BBP<sup>3</sup> exposed for 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm<sup>2</sup>. The oxygen scavenging was tested with 300 cc air at room temperature. The O<sub>2</sub> uptake capacity is based on total weight of the 3-layer film. The results of the tests are given below in Table 8. These results are plotted along with the results of Example 9 in Figure 4, which graphically plots % oxygen in headspace against time (days).

1

Table 8

Time (days)	Head-space O <sub>2</sub> (Vol%)	Head-space O <sub>2</sub> Vol, (ml)	Vol-O <sub>2</sub> Used (ml)	O <sub>2</sub> Uptake (ml/g)	O <sub>2</sub> Uptake Avg Rate (cc/m <sup>2</sup> ·day)	Instant Rate (cc/m <sup>2</sup> ·day)	O <sub>2</sub> Capacity (cc/m <sup>2</sup> )
0.0	20.60	61.80	0.00	0.00	0.0	0.0	0.0
1.0	17.70	52.21	8.56	18.20	426	426	428
2.0	17.40	50.46	9.43	20.05	235	43	471
3.0	17.10	48.74	10.28	21.87	174	45	514
6.2	17.10	47.88	10.28	21.87	83	0.0	514

2

3

Example 14

4

Taste Preference Test

5 The organoleptic quality of a film containing EMCM as the scavenging resin in  
6 a multi-layer oxygen scavenging packaging structure was evaluated and  
7 compared with an SBS (styrene/butadiene/styrene)-based oxygen scavenging  
8 packaging structure. Films were triggered with 800 mJ/cm<sup>2</sup> of 254 nm UV.  
9 Packages containing ca. 200 ml of water were made and vacuum/gas flushed  
10 to obtain a gas composition of 1% O<sub>2</sub>:99% N<sub>2</sub>. Packages were stored at 40°F  
11 for seven days prior to taste testing. A forced preference double blind  
12 Triangle taste test was carried out on water extracts of the EMCM-based and  
13 SBS-based films.

14 Sensory results indicated that there was a significant difference (24 out of 28  
15 respondents) between the EMCM-based and SBS-based structures. All 24  
16 respondents who correctly identified the odd sample in the single test  
17 preferred the taste of the water packaged in EMCM over SBS. As shown in  
18 Table 9, Day 4 scavenging rates of the EMCM-based structures were lower  
19 than the SBS counterpart. On Day 4, both structures had significant oxidation  
20 and the obvious difference in flavor perception was attributed to the fewer and

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1 less objectionable by-products (fragments after oxidation of EMCM) of the  
2 EMCM oxygen scavenging system.

3 In a second forced preference triangle taste test, water samples in  
4 EMCM-based scavenging structures were tested against water samples  
5 packaged in a standard barrier laminate film (R660B manufactured by  
6 Cryovac Division of Sealed Air Corporation). The packaged water extract  
7 samples were submitted to a sensory panel for forced preference double blind  
8 taste testing. Samples were tested after 8 days of scavenging. A significant  
9 difference in the taste was found between the samples packaged in the  
10 EMCM and the control packages. Surprisingly, the preference was towards  
11 the EMCM structure. Open comments stated that there was no off-flavor  
12 (normally associated with the SBS-based oxygen scavenging films) in the  
13 EMCM samples and that EMCM was "pretty close in taste to the control."  
14 Headspace oxygen levels reached by the EMCM structure were ca. 0.2%  
15 (down from 1%) at Day 8. Scavenging results of the EMCM film used during  
16 this test are also listed in Table 9.

17 Table 9  
18 Oxygen Scavenging  
19 Packaging Films

Film Sample	Average Rate (cc/m <sup>2</sup> ·day)	Average Rate (cc/m <sup>2</sup> ·day)	Induction Period (days)	Peak Instantaneous Rate avg. (c) (cc/m <sup>2</sup> ·day)	Peak Instantaneous Rate (cc/m <sup>2</sup> ·day)
	Mean	St. dev.		Mean	St. dev.
SBS Film	51.0 <sup>a</sup>	7.8	<1	88.4 (1)	14.1
1 <sup>st</sup> Sensory test EMCM	41.6 <sup>a</sup>	5.3	<1	68.6 (2)	11.4
2 <sup>nd</sup> Sensory Test EMCM	30.5 <sup>b</sup>	5.9	<1	83.6 (2-3)	19.4

20 <sup>a</sup>Rate at 4 days.

21 <sup>b</sup>Rate at 8 days.

22 <sup>c</sup>Time to reach peak rate in days.

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Example 15

Taste Preference Test

Oxygen scavenging test films, 5 cm x 20 cm, were irradiated with 800 mJ/cm<sup>2</sup> ultraviolet (254 nm) and heat tacked to the top of the test pouches (one per pouch). The pouches (16 cm x 19 cm) were made from laminated barrier film specifically designed to be oxygen impermeable. 21 gram slices of freshly sliced turkey roll were put into sterilized 9 cm petri dishes (one per dish). The dishes were, in turn, placed into the barrier pouches (one per pouch). The pouches were heat sealed, filled with 300 cc 1% oxygen/99% nitrogen gas, and stored at 4°C for the duration of the test.

Two types of oxygen scavenging polymers were compared in the test against a control (barrier pouch alone, no oxygen scavenger). The oxygen scavenging films were each three layer (ABA) structures in which the outer, "A", layer was 0.5 mil thick LLDPE, and the middle, "B", layer was 1.0 mil thick oxygen scavenging polymer (compounded with 1000 ppm cobalt (as oleate) and 1000 ppm of a photoinitiator (BBP<sup>3</sup>). The headspace oxygen for the pouches is shown in Table 10. Both of the test oxygen scavenging films scavenged more oxygen than the packaged turkey itself.

Table 10

Oxygen scavenging layer composition	Initial headspace oxygen, %	Headspace oxygen after 3 days @ 4°C, %
none	1.02	0.72
SBS	1.00	0.08
EMCM	1.02	0.17

Taste panelists were instructed to force rank the samples according to their taste preference; assigning the least preferred sample a score of 1, and the most preferred sample a score of 10. As is shown in Figure 5, the panelists

1 found the taste of the turkey packaged in control and the EMCM pouches  
2 statistically equivalent. The turkey packaged in the SBS pouch was found  
3 significantly less preferred than either the control or the EMCM.

4 Example 16

5 Polymerization of EMCM via high pressure autoclave reactor proceeds in a  
6 steady-state continuous manner as follows. Ethylene is circulated at a rate of  
7 10,000-14,000 lb/hr by a hypercompressor which compresses the ethylene to  
8 16,500-22,500 psig. The compressed ethylene is injected into the autoclave  
9 reactor in various positions along the reactor wall associated with the zone  
10 divisions made by the reactor internals. Simultaneously, acrylate of  
11 cyclohexene-1-methanol (CHAA) comonomer is injected into either the first  
12 zone or the first and second zones of the reactor at a rate sufficient to  
13 produce a copolymer containing from 5 to 40% CHAA, more typically  
14 10%-25% by weight. The reaction is initiated by injection of a solution of  
15 di-tert butyl peroxy-pivalate in an aliphatic solvent which also functions as a  
16 chain transfer agent. The initiator is injected at a rate to provide  
17 approximately 10-20 ppm (wt) of initiator in the compressed ethylene.

18 The locations of the CHAA injection are critical to the polymer being  
19 produced, as is shown in U.S. Patent No. 5,571,878 which details the effects  
20 of acrylate injection location on the polymerization of ethylene and an alkyl  
21 acrylate comonomer in a high pressure system.

22 The resultant polymer exits the reactor at a rate of 1000-2000 lb/hr in a  
23 multi-phase solution in ethylene to a high pressure separator. The pressure  
24 of the product is reduced adiabatically through a valve to 2,000 psig pressure  
25 and the unreacted ethylene and unreacted CHAA are recompressed to  
26 reactor pressure and reinjected into the reactor for further polymerization.  
27 Additional ethylene is added to the cycle via a primary compressor which

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1 compresses the ethylene from pipeline pressure to the suction pressure of the  
2 hypercompressor at a rate equal to the polymer production rate.

3 From the high pressure separator, the polymer is reduced in pressure to  
4 4-10 psig for further removal of unreacted ethylene and unreacted  
5 comonomer. The polymer is fed into a melt pumping device (either an  
6 extruder or a gear pump) and is pelletized and transferred for packaging and  
7 shipment.

8 Although a few embodiments of the invention have been described in detail  
9 above, it will be appreciated by those skilled in the art that various  
10 modifications and alterations can be made to the particular embodiments  
11 shown without materially departing from the novel teachings and advantages  
12 of the invention. Accordingly, it is to be understood that all such modifications  
13 and alterations are included within the spirit and scope of the invention as  
14 defined by the following claims.

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